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# Final Research Report:

*"Quantum Dynamics of Helium Clusters"*

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## Introduction

Our study of helium clusters was motivated by the desire to understand the scaling of the unusual properties of bulk $^4He$, a quantum liquid, in finite size systems as one goes from the macroscopic regime to the regime of molecular dimensions. This is fully in the spirit of general cluster research, namely to develop our understanding of how the transition from molecular to bulk systems (or vice versa) is reflected in the internal structure and dynamics of finite size aggregates. The unique feature of helium is its dominant quantum behavior, resulting from a low mass and weak interatomic binding energy. Clusters of helium are therefore very weakly bound van der Waals species, whose properties are expected to be dominated by zero point delocalization effects. During this grant period, we devoted our attention exclusively to clusters of $^4He$, which are Bose systems. These are more strongly bound than the fermionic species $^3He_N$, and are also easier and cheaper to study experimentally. Furthermore, analogy with the bulk behavior suggests that any superfluid effects, if present, will occur at considerably higher and therefore more experimentally accessible temperatures for $^4He_N$.

## Goals of original research plan

1 ) To understand the size-dependent scaling of superfluid behavior or analogous collective effects in clusters of $^4He_N$. As a preliminary step this involved analysis of Bose-Einstein condensation in a weakly interacting Bose cluster.

2 ) Despite much phenomenological progress in the understanding of superfluidity in bulk helium II, a molecular description for the characteristic excitations of bulk helium found only in the superfluid state was still missing. By developing a truly microscopic theory of collective excitations in these quantum clusters based on accurate ground and excited state wavefunction information, we aimed to achieve new insight into the atomic dynamics underlying the superfluid state in bulk He II by identifying and analyzing the behavior in finite sized clusters.

3 ) Determination of feasible experimental probes of the cluster dynamics, in particular of charged species or of non-dissociative molecular probes. This goal is further related to the more long term aim of employing the unusual physical properties of these quantum clusters to modify and control the course of chemical reactions of embedded/attached species at ultra-low temperatures.

4 ) Development of Monte Carlo methods to provide accurate ground and excited state wavefunctions for the $^4He_N$ clusters.

## Goals achieved during grant period

Our central achievements attained during the grant period are the following:

1 ) Establishment of a new quantum liquid drop theory for the collective excitations of these Bose clusters, (papers 1, 2, 4). Together with the accurate ground state wavefunctions described below, this led to calculations of the compressional excitation spectrum for $l = 0$ (spherical) and $l = 1$ (dipole) symmetries, for a range of cluster sizes. The size scaling of the excitation spectrum showed the onset of a roton minimum at sizes $N \sim 70$, leading to the important physical conclusion that clusters of size $N \geq 70$, corresponding to diameters $R \geq 10$ Å can support superfluid flow.

2 ) Development of accurate Monte Carlo methods for ground state wavefunctions of general quantum clusters (papers 5, 8). These consisted of both variational and (exact) diffusion Monte Carlo techniques. While the basic 'unguided' Metropolis sampling of variational cluster wavefunctions had been previously employed by the nuclear physics community, we improved the accuracy and sampling techniques considerably, by developing new variational wavefunction forms and using guiding functions to optimize sampling at small interparticle separations. This resulted in an unprecedented precision of ~ 5% in density profiles in the interior of the cluster, and led to an unexpected discovery of a large collinear contribution to the structure of the $He_3$ trimer (paper 7). Application of diffusion Monte Carlo to these weakly bound atomic systems is new, and was perfomed selectively to calibrate the variational results (paper 8). These exact calculations show structure in both density profiles and pair distribution functions which is compatible with weak hard-core packing effects. No such structure is observed at the variational level.

3 ) Development of a quantum theory for atomic and molecular impurities in helium clusters (paper 7). This has so far been restricted to ground state impurities, and consists of a variational approach to the new cluster containing the impurity, in which the latter interacts pairwise with the helium atoms. The variational wavefunction is extended to include pairwise correlation terms between the impurity and the helium. This approach has been applied to a $H_2$ impurity attached to $He_N$, $N = 2 - 19$, and structural analysis of the resulting mixed cluster ground state has been made. The lighter impurity $H_2$ is extensively delocalized throughout the cluster, with a peak in the vicinity of the diffuse surface region. Quantitative analysis showed that the $H_2$ is however still largely in the interior of the cluster for this range of sizes. The $H_2 He_{13}$ species is unique in the extent to which it expels the $H_2$, suggesting an unusual structural stability which may be associated with an icosahedral $He_{13}$ unit. This is particularly significant in light of the absence of any energetic magic numbers for neutral helium clusters.

This ground state theory for impurities now enables us to calculate spectral shifts of impurity absorption lines due to, e.g., dipole-induced dipole interactions with the surrounding 'solvent' helium species. Comparison with recent experimental measurements of such shifts for $SF_6$ in $He_N$ is underway.

4 ) Development of quantum theoretical approaches to excited states for the collective modes (papers 2, 5). This began with a variational approach to excited compressional states which was based on the Feynman operator approach, and has recently been extended to excited states of overall rotation of the cluster. The first four excited compressional states were calculated variationally for N = 240, maintaining orthogonality to lower states by a generalized Gramm-Schmidt procedure. These results showed a significant lowering of the compressional energies relative to both classical estimates based on the conventional macroscopic liquid drop model, and also to our new quantum liquid drop model. Study of rotationally excited states of the cluster are now underway with the aim of analyzing centrifugal distortions of rotating clusters.

5 ) The ground and excited state Monte Carlo techniques developed for helium clusters have also been applied to clusters of $H_2$ (j = 0), which is also a Bose system (paper 6). We introduced an additional element of employing 'shadow wavefunctions' for fictitious particles representing lattice sites here in order to allow for more rigid structures. The primary goal of this extension of our helium studies is to determine whether a liquid-like ground state exists for $(H_2)_N$ for N small, and if so, whether these clusters display similar superfluid behavior to $He_N$. Our first results show that the smallest clusters ($N \leq 7$) are extensively delocalized,. Clusters up to N = 33 still show strong delocalization, although weak features characteristic of solid-like close packed structures are now also apparent.

## Publications resulting from grant


1. M.V. Rama Krishna and K. B. Whaley, "Collective Excitations of Helium Clusters," Phys. Rev. Lett. **54**, 1126 (1990).

2. M.V. Rama Krishna and K.B. Whaley, "Microscopic Studies of Collective Spectra of Quantum Liquid Clusters" J. Chem. Phys. **93** ,746 (1990).

3. M.V. Rama Krishna and K. B. Whaley, "Superfluidity in Helium Clusters" in "*On Clusters and Clustering: from Atoms to Fractals*", (North Holland, 1991).

4. M.V. Rama Krishna and K.B. Whaley, "Structure and Excitations of Quantum Liquid Clusters" invited article, Modern Physics Letters B **14**, 895 (1990).

5. M.V. Rama Krishna and K.B. Whaley, "Wavefunctions of Helium Clusters", J. Chem. Phys. **93**, 6738 (1990).

6. M.V. Rama Krishna and K. B. Whaley, "The Structure of Small Molecular Hydrogen Clusters", Z. Phys. D., **20**, 223 (1991).

7. R.N. Barnett and K.B. Whaley, "Monte Carlo Study of Impurities in Quantum Clusters: $H_2{}^4He_N$, N=2-19" (J. Chem Phys., in press Feb. 15, 1992)

8. R.N. Barnett and K.B. Whaley, "Variational and Exact Monte Carlo Techniques for Quantum Clusters" (Phys. Rev. A, submitted)